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14. ABSTRACT
This slide presentation presents the results of work completed to evaluate analytical data related to fuels weathering (primarily JP-4). The companion report, "Light Nonaqueous-Phase Liquid (LNAPL) Weathering at Various Fuel Release Sites" was completed Sep 1999. The data set was used to form a robust database for estimating fuel LNAPL weathering rates.

The study focused primarily on the weathering or natural depletion of BTEX components from free-phase product.

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Weathering of JP-4 LNAPL Hydrocarbons and Implications for Risk-Based Site Closures and Monitored Natural Attenuation

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Introduction

This presentation presents the results of work completed to evaluate natural weathering of light nonaqueous-phase liquids (LNAPLs) resulting from petroleum releases to the subsurface environment. Of particular interest for this study was the weathering, or natural depletion, of benzene, toluene, ethylbenzene, and xylenes (BTEX) from free-phase product (i.e., mobile LNAPL) following a JP-4 jet fuel release.

Problem Statement

Little information is available regarding natural weathering rates of the BTEX components from mobile fuel LNAPLs. As a result, contaminant source-term reduction rates in groundwater models are left to professional judgment, with little, or no, basis.

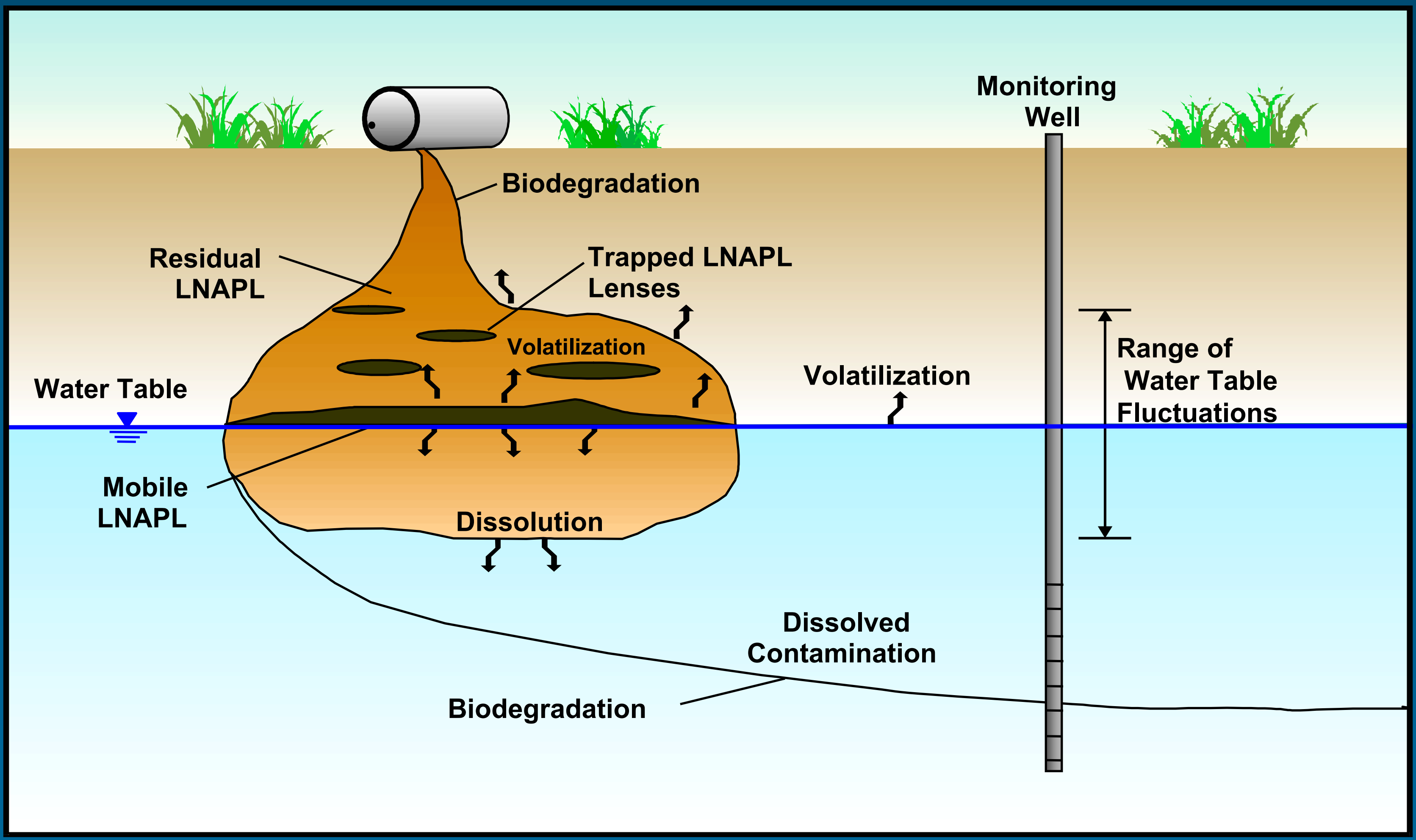
Implications

- Overly conservative LNAPL weathering rates negatively impact feasibility and cost of implementing monitored natural attenuation (MNA).
- Overestimation of weathering rates can lead to an overly optimistic forecast of MNA performance.
- A default value of 5 percent per year (%/yr) often has been assumed, but with no scientific validation.

Project Objective

Improve the scientific basis of, and defensibility for, natural LNAPL weathering rates (i.e., contaminant source-term reduction rates).

LNAPL Weathering Conceptual Model



LNAPL Weathering Mechanisms

- The primary mechanisms acting to reduce the strength of the LNAPL source are:
  - Dissolution
  - Volatilization
  - Biodegradation
- These mechanisms are influenced by physical and chemical properties of the compounds in the source product, as well as by physical, chemical, and biological properties of the soil and groundwater system.

Site Selection Criteria

Identifying sites that met all of the criteria listed below proved to be difficult; therefore, the criteria were used as guidelines for site selection:

1. Presence of recoverable mobile JP-4 LNAPL in the subsurface

2. Known date of fuel release

3. Single release confined to a relatively short period of time

Site Selection Criteria (continued)

4. Minimal site remediation

5. Historic LNAPL analytical results for BTEX

6. Depth to groundwater less than 40 feet bgs

7. DOD sites

JP-4 Release Site Summary

Five JP-4 sites, with spill ages ranging between approximately 4 and 24 years, were included in the study.

Site/Location	*Date of Release*	*Amount Released (gallons)*	*Soil Type*
Bldg 1610 Shaw AFB, SC	June 1994	Unknown	Sand
Pipeline Leak Site Myrtle Beach AFB, SC	January 1981	123,000	Clay/Sand
Tank 1 Area, DFSP Charleston, Hanahan, SC	October 1975	83,000	Clay/Sand
Spill Site No. 2 Eaker AFB, AR	October 1973	Unknown	Sandy Silt
Washrack/Treatment Area McChord AFB, WA	1975	100,000	Silty Gravel

JP-4 Release Site Summary (continued)

Five JP-4 sites, with spill ages ranging between approximately 4 and 24 years, were included in the study.

Site/Location	Depth to Water Table (feet bgs)	Groundwater Velocity (feet/year)	Free Product Thickness (feet) and Date
Bldg 1610 Shaw AFB, SC	29-33	400	2.5 (8/96)
Pipeline Leak Site Myrtle Beach AFB, SC	2-8.5	420	3.79 (11/95)
Tank 1 Area, DFSP Charleston, Hanahan, SC	18-22	62	1.77 (5/96)
Spill Site No. 2 Eaker AFB, AR	8-14	16	1.18 (8/97)
Washrack/Treatment Area McChord AFB, WA	11-15	NA	0.14 (4/94)

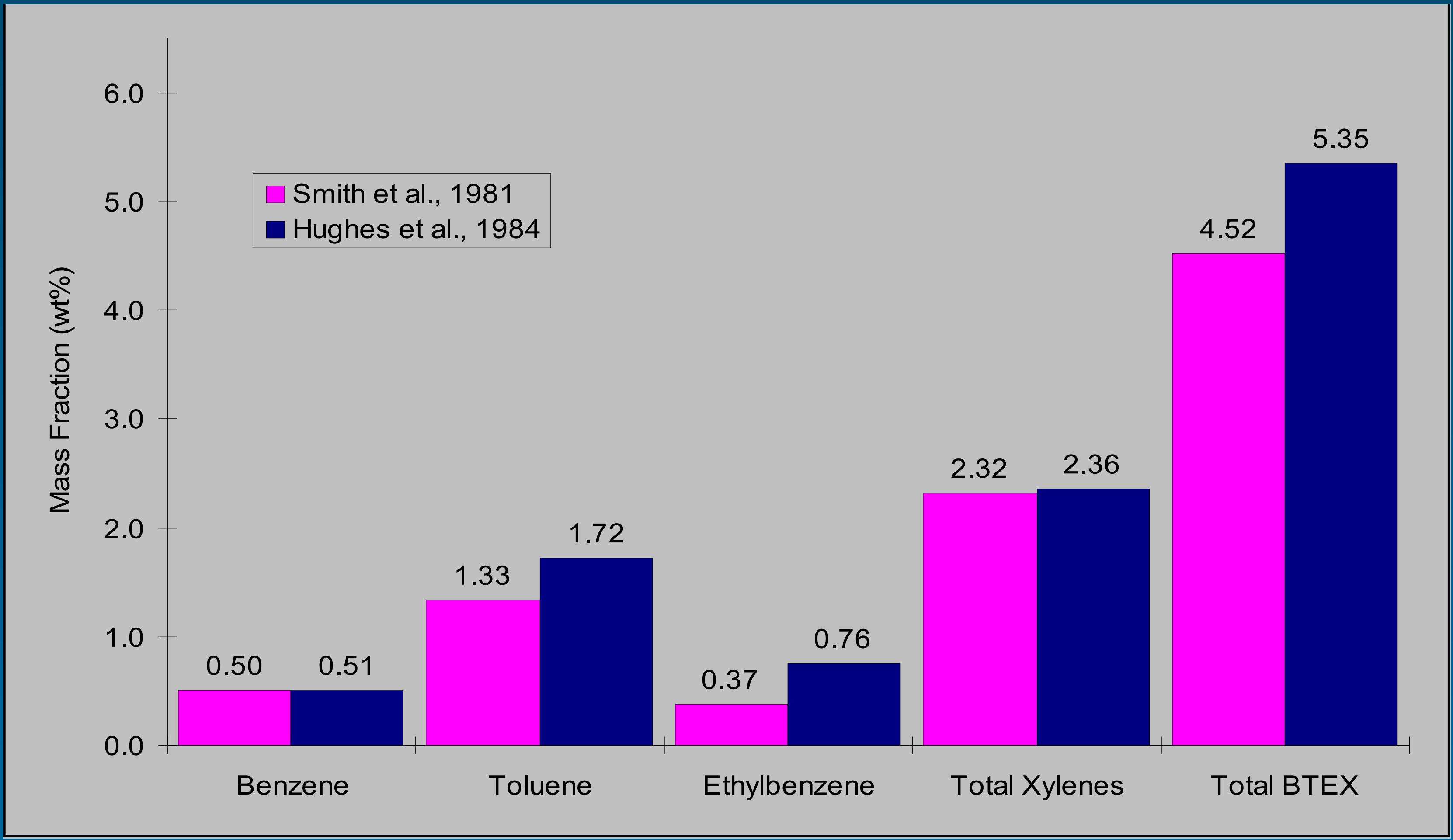
Sample Collection and Analysis

Soil, groundwater, and LNAPL samples were collected and analyzed for BTEX and naphthalene

BTEX Weathering in JP-4 LNAPL

- To estimate weathering rates, the following must be known:
  - Initial BTEX concentrations in fresh JP-4
  - Date of fuel release
  - Date of sampling event

BTEX Composition in Fresh JP-4



Individual Site Data

- Using the known dates of the product release and the assumed initial BTEX composition, the degree of mobile LNAPL weathering (i.e., BTEX mass fraction depletion) that has occurred with time was determined for each release site.
- Minimum, maximum, and average annual contaminant reduction rates, assuming zero-order and first-order weathering at the five JP-4 sites, were calculated.

Site Specific BTEX Weathering Rates in JP-4 Mobile LNAPL

Site Analyte	Approximate Spill Age	Zero Order (%yr)			First Order (%yr)		
		min	max	avg	min	max	avg
Shaw AFB, SC Total BTEX	4 years	14	24	18	16	33	23
Myrtle Beach AFB, SC Total BTEX	16 years	4.6	5.7	5.1	8.3	14	11
DFSP-Charleston, SC Total BTEX	22 years	3.7	5.2	4.3	6.7	18	11
Eaker AFB, AR Total BTEX	24 years	0.0	3.3	1.7	0.0	6.1	2.9
McChord AFB, WA Total BTEX	22 years			4.5			43

Site Specific Benzene Weathering Rates in JP-4 Mobile LNAPL

Site Analyte	*Approximate Spill Age*	*Zero Order (%yr)*			*First Order (%yr)*		
		min	max	avg	min	max	avg
Shaw AFB, SC Benzene	4 years	11	23	17	12	31	22
Myrtle Beach AFB, SC Benzene	16 years	5.8	6.1	5.9	16	23	19
DFSP-Charleston, SC Benzene	22 years	4.6	5.5	4.8	14	43	35
Eaker AFB, AR Benzene	24 years	2.0	4.2	3.1	2.7	26	12
McChord AFB, WA Benzene	22 years			4.5			42

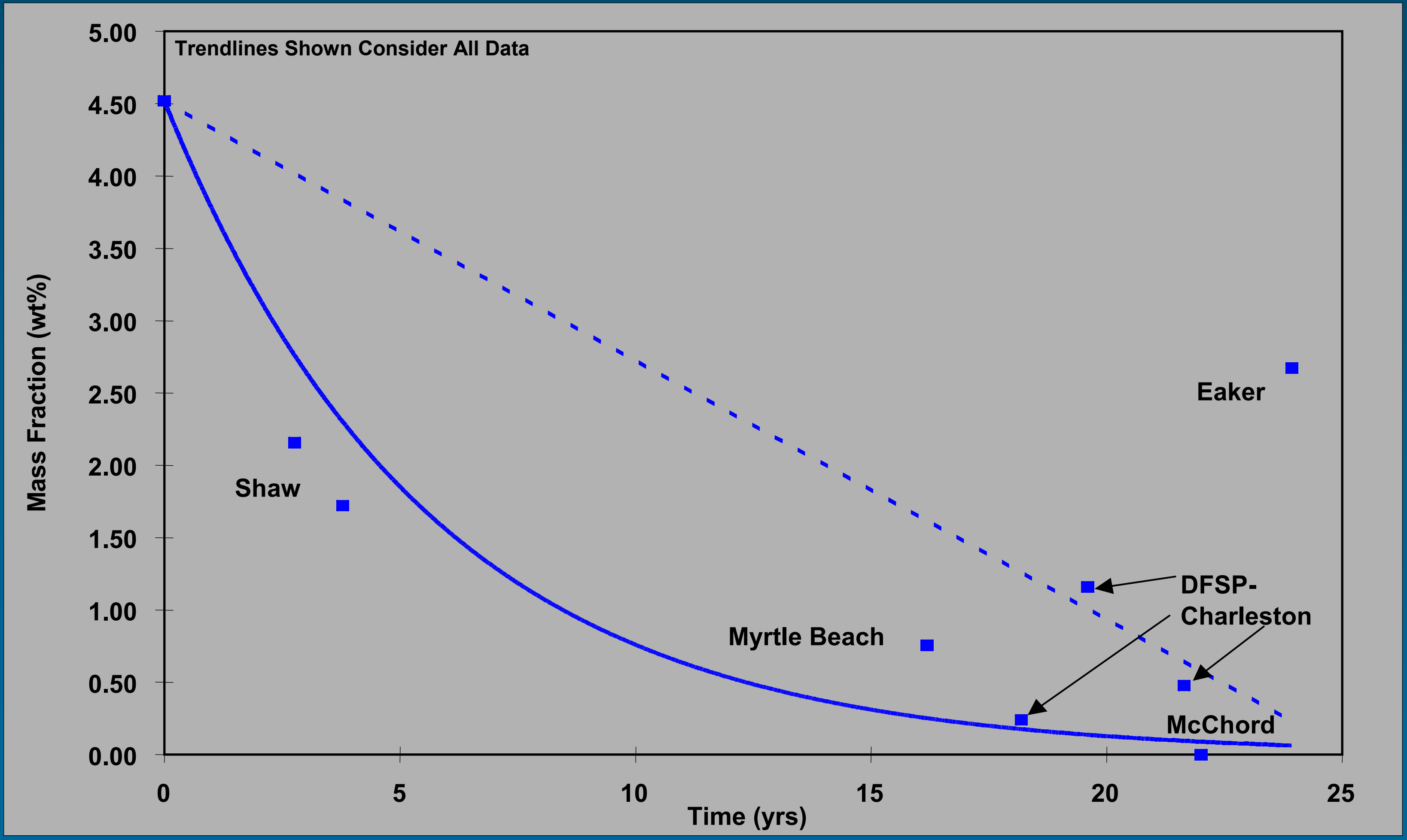
Site Specific BTEX Weathering Rates in JP-4 Mobile LNAPL

- No BTEX was detected in the one LNAPL sample from the McChord AFB site.
- Low reduction rates at the Eaker AFB site likely are the result of a more recent, undocumented, fuel release.

Combine JP-4 Site Data to Assess Weathering Rates

- **Data from all five JP-4 sites were compiled to evaluate the relationship between BTEX depletion in mobile JP-4 LNAPL and spill age.**
- **Calculate total BTEX and benzene weathering considering average data from the JP-4 release sites**

Total BTEX Weathering Considering Average Data



Total BTEX Weathering Considering All Data

Zero-Order

Best Fit Curve: $y = -0.1795x + 4.52$

$R^2 = 0.0248$

Weathering Rate = 4.0%C_o per year

First-Order

Best Fit Curve: $y = 4.52e^{-0.1783x}$

$R^2 = 0.1829$

Weathering Rate = 16.3% per year

Total BTEX Weathering Considering All Data Except Eaker

Zero-Order

Best Fit Curve: $y = -0.2095x + 4.52$

$R^2 = 0.4428$

Weathering Rate = 4.6%C_o per year

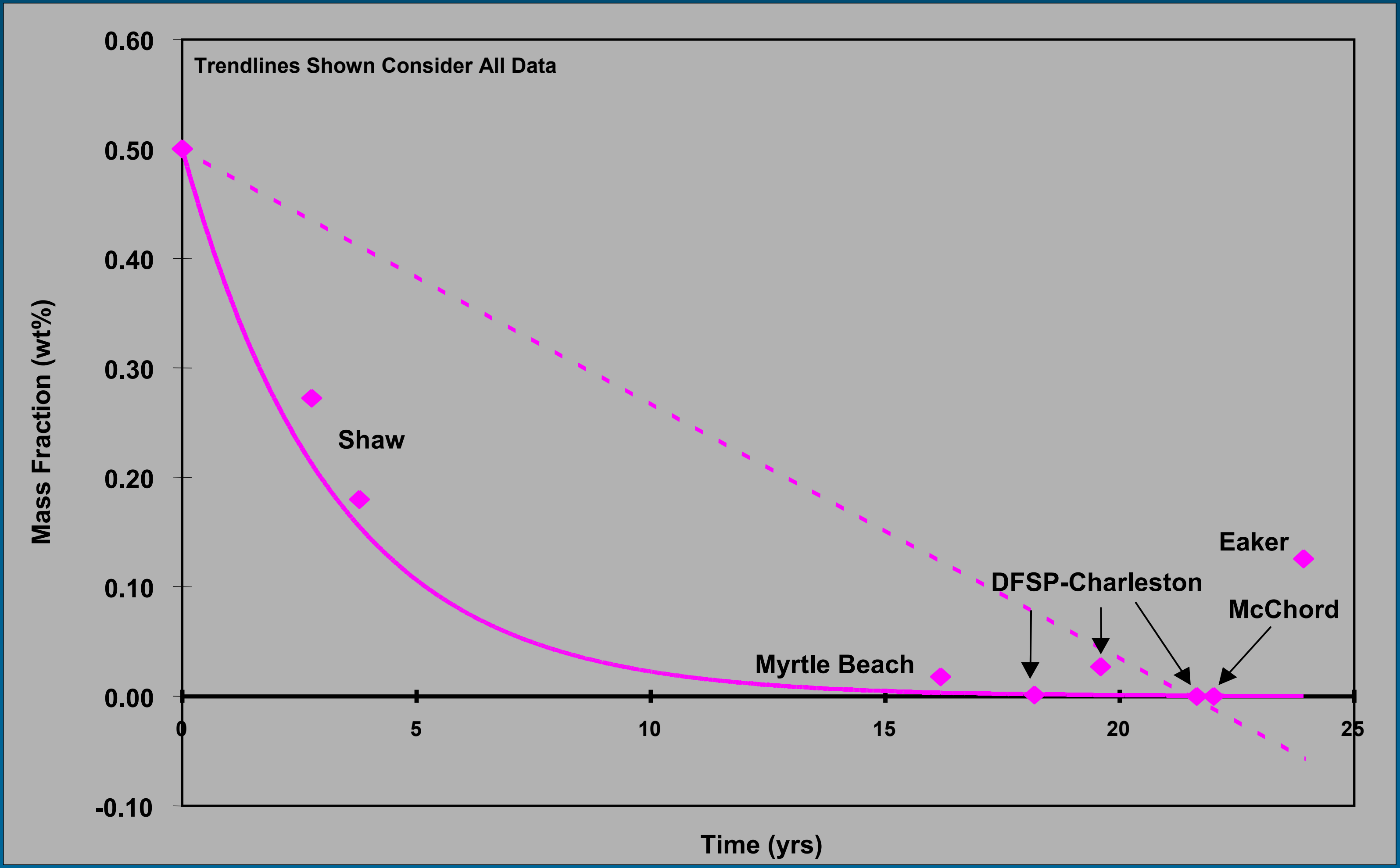
First-Order

Best Fit Curve: $y = 4.52e^{-0.2242x}$

$R^2 = 0.3104$

Weathering Rate = 20% per year

Benzene Weathering Considering Average Data



Benzene Weathering Considering All Data

Zero-Order

Best Fit Curve: $y = -0.0233x + 0.50$

$R^2 = 0.4368$

Weathering Rate = 4.7%C_o per year

First-Order

Best Fit Curve: $y = 0.50e^{-0.3099x}$

$R^2 = 0.4063$

Weathering Rate = 26.7% per year

Benzene Weathering Considering All Data Except Eaker

Zero-Order

Best Fit Curve: $y = -0.0255x + 0.50$

$R^2 = 0.6221$

Weathering Rate = 5.1% C_o per year

First-Order

Best Fit Curve: $y = 0.50e^{-0.3839x}$

$R^2 = 0.6548$

Weathering Rate = 31.9% per year

Dissolution Dominated Weathering

- As mobile LNAPL concentrations decrease, compound depletion rates decrease (in accordance with Raoult's Law).
- Benzene and toluene weathering rates generally are higher than ethylbenzene and xylene weathering rates (because of their higher effective water solubilities).

Dissolution Dominated Weathering (continued)

- **Under equilibrium conditions, lower groundwater velocities create a lower dissolution flux for mobile LNAPL depletion.**
  - The lowest weathering rates were observed at the Eaker AFB site (groundwater velocity approximately 16 feet per year).
  - Higher BTEX depletion rates were observed at the other sites possibly because of higher groundwater velocities and/or precipitation rates.

Conclusions

1. BTEX weathering rates in free-phase fuel, or mobile LNAPL, will vary from site to site and are influenced by:
   - Spill age
   - Solubility and LNAPL concentration of individual compounds
   - Free product geometry
   - Groundwater and precipitation rates

Conclusions (continued)

2. The BTEX fraction remaining in free-phase LNAPL samples collected from different locations on the same site will vary.
   – Samples from the center of the LNAPL "plume" will exhibit lower rates of weathering
   – A site average based on multiple samples is recommended

Conclusions (continued)

3. Weathering of BTEX from LNAPL is expected to follow first-order kinetics in accordance with Raoult's Law
4. Average first-order total BTEX weathering in JP-4 mobile LNAPL
   - Range: 11 – 23%/yr (excluding McChord and Eaker data)
   - Recommended default: 16%/yr
   - Conservative default: 11%/yr

Conclusions (continued)

5. Because benzene is a known human carcinogen with a federal MCL of 5 µg/L, benzene weathering rates will generally determine the timeframe for fuel spill remediation.
6. Average first-order benzene weathering in JP-4 mobile LNAPL
   – Range: 19 – 35%/yr (excluding McChord and Eaker data)
   – Recommended default: 26%/yr
   – Conservative default: 19%/yr

Conclusions (concluded)

7. Dissolution appears to be the primary weathering mechanism that influences mobile LNAPL weathering rates. Significantly lower BTEX weathering rates in mobile LNAPL were apparent at sites with low groundwater velocities.